

Supplementary Material

1. The Force Field

We used the DREIDING force field described in Ref. 8: S.S. Jang, V. Molinero, T. Cagen, W.A. Goddard III “Nanophase-Segregation and Transport in Nafion 117 from Molecular Dynamics Simulations: Effect of Monomeric Sequence” J. Phys. Chem. B 108 (2004) 3149-3157. Charges of all atoms were calculated using the charge equilibration method.

$$E_{\text{vdW}}(R) = D_0 \left\{ \left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right\}, E_Q^a = 322.0637 \sum_{i>j} \frac{Q_i Q_j}{\epsilon R_{ij}}$$

$$E_{\text{bond}}(R) = \frac{1}{2} K_b (R - R_0)^2, E_{\text{angle}}(\theta) = \frac{1}{2} K_\theta (\theta - \theta_0)^2$$

$$E_{\text{torsion}}(\phi) = \sum_n \frac{1}{2} V_n [1 - d_n \cos(n\phi)]$$

E_{vdW}	¹ H(HF3C), ² H(HH3O)	R_0^c	0.9000	D_0^d	0.0100
	¹ O(OF3C), ² O(OH3O)	R_0	3.5532	D_0	0.1848
	¹ C(C_3T) ^b	R_0	3.8837	D_0	0.0844
	² C(C_3)	R_0	3.8983	D_0	0.0951
	¹ F(F_3), ² F(F_3) ^b	R_0	3.3953	D_0	0.0496
	³ H(H_A)	R_0	3.1950	D_0	0.0001
	³ O(O_3), ⁴ O(O_2),	R_0	3.4046	D_0	0.0957
	S(S_3)	R_0	4.0300	D_0	0.3440
E_{bond}	OF3C – HF3C	R_0	1.0000	K_b^e	500.0000
	OH3O – HH3O	R_0	0.9820	K_b	1085.9565
	C_3T – C_3T	R_0	1.4982	K_b	429.3204
	C_3 – C_3	R_0	1.5300	K_b	700.0000
	C_3T – C_3	R_0	1.5300	K_b	700.0000
	C_3 – O_3	R_0	1.4200	K_b	700.0000
	C_3(T) – F_3(3)	R_0	1.3360	K_b	605.2595
	C_3 – S_3	R_0	1.8000	K_b	700.0000
	S_3 – O_3	R_0	1.6900	K_b	700.0000
	S_3 – O_2	R_0	1.4800	K_b	700.0000
E_{angle}	O_3 – H_A	R_0	0.9800	K_b	700.0000
	HF3C–OF3C–HF3C	θ_0^f	109.4700	$K_{\theta g}$	120.0000
	HH3O–OH3O–HH3O	θ_0	113.4000	K_θ	79.0263
	X – C_3(T)–X	θ_0	109.4710	K_θ	100.0000
	C_3(T)–C_3(T)–C_3(T)	θ_0	122.5536	K_θ	106.2739
	C_3(T)–C_3(T)–F_3(3)	θ_0	118.3191	K_θ	100.3366
	F_3(3) – C_3(T) – F_3(3)	θ_0	121.5020	K_θ	108.2396
	X – S_3 – X	θ_0	109.4710	K_θ	350.0000
E_{torsion}	O2 – S_3 – O2	θ_0	115.5000	K_θ	350.0000
	X – C_3(T) – C_3(T) – X	$V_3(d_3)^h$	2.0000 (–1)		
	C_3T–C_3T – C_3T – C_3T	$V_3(d_3)$	6.4342 (1)		
	F_3(3)–C_3T – C_3T – C_3T	$V_3(d_3)$	8.2444 (1)		
	F_3(3)–C_3T – C_3T – F_3(3)	$V_3(d_3)$	8.0848 (–1)		
	X – C_3(T) – O_3 – X	$V_3(d_3)$	2.0000 (–1)		
	X – C_3(T) – S_3 – X	$V_3(d_3)$	2.0000 (–1)		
	X – S_3(T) – O_3 – X	$V_2(d_2)$	2.0000 (–1)		

The force field was tested for the en masse diffusion and OH-hydration shell in pure water and reasonable results were obtained. The coordination number of OH is about 5 if OH-H₂O distances up to 3.5 Å are included. This is consistent with neutron scattering experiments [17, 18], according to which the hydroxide-ion can accept between 3 and 4 hydrogen bonds and donate one (the longest) in aqueous environment.

The diffusion coefficient for en masse diffusion is frequently approximated by the self diffusion coefficient of water which has been reported to be $\sim 2 \cdot 10^{-5}$ cm²/sec [see, for instance, Ref.16 and M.E. Tuckerman, A. Chandra, D. Marx, Accounts of Chemical Research 39 (2006) 151-158]. Our calculated value is about $0.6 \cdot 10^{-5}$ cm²/sec which is lower than the experimental value but in very good agreement with calculated values obtained using three popular density functionals, PW91, BLYP, and HCTH [M.E. Tuckerman, A. Chandra, D. Marx, Accounts of Chemical Research 39 (2006) 151-158], 0.30, 0.25, and $0.64 \cdot 10^{-5}$ cm²/sec, respectively.

2. Mean Square Displacement (MSD) and line fit to MSD

Diffusion coefficients were calculated based on the MSD:

$$\text{MSD}(m) = \langle |r(t) - r|^2 \rangle = 1/n \sum_{i=1}^n |r(m+i) - r(i)|^2$$

where r is the position of the particle, t is the time, k is the total number of snapshots ($k = m+n > 0$), m is the maximum number of points allowed for the MSD calculation ($m = k/2$ in our calculations), n is the number of data points used for averaging, and i is the step counter.

The self-diffusion constant is obtained using the Einstein relation:

$$D = \frac{1}{6Nt} \langle |r(t) - r|^2 \rangle$$

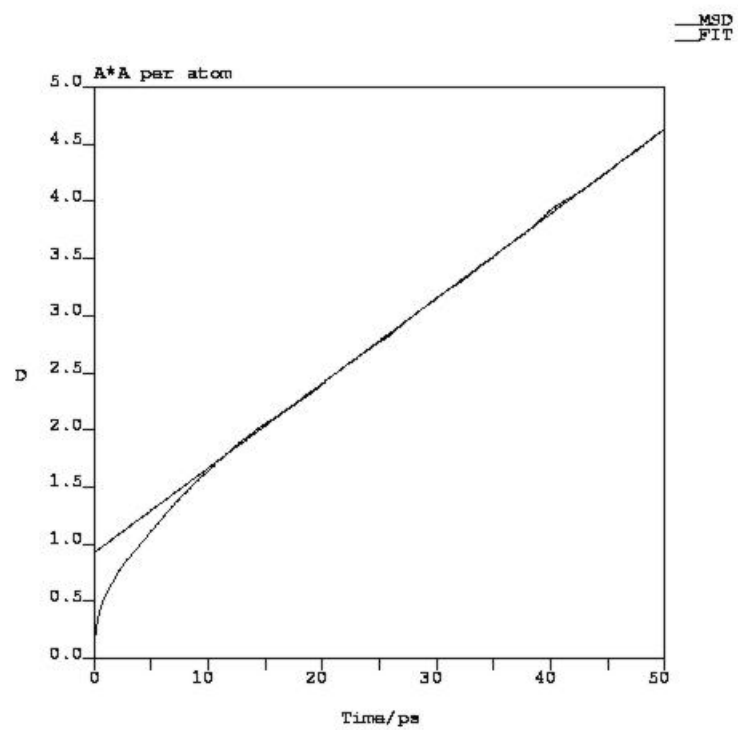
where N is the number of atoms. We fitted the temperature dependence of the diffusion coefficient to

$$D(T) = D_0 \exp(-E_a/kT)$$

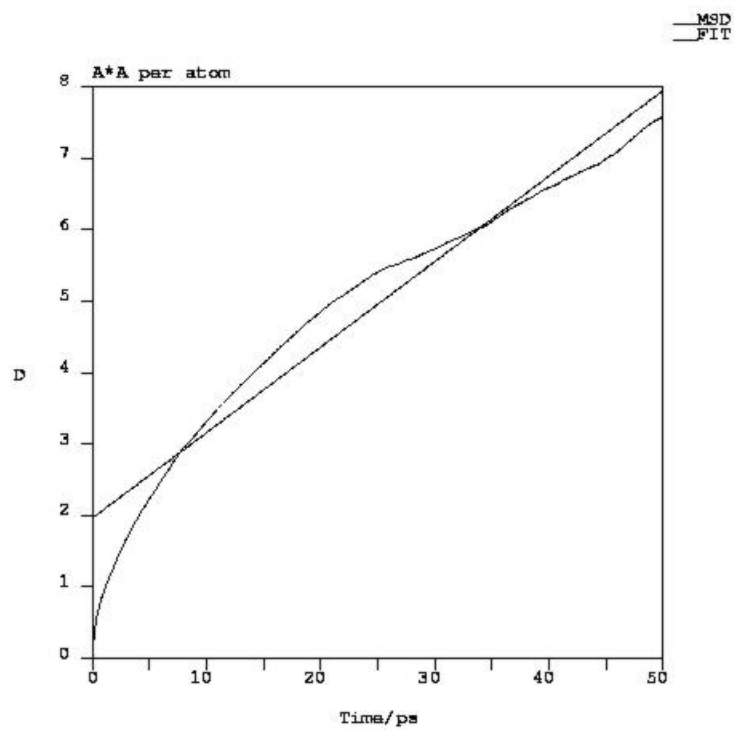
where E_a is the activation enthalpy.

2.1. QAPS-OH dry membrane:

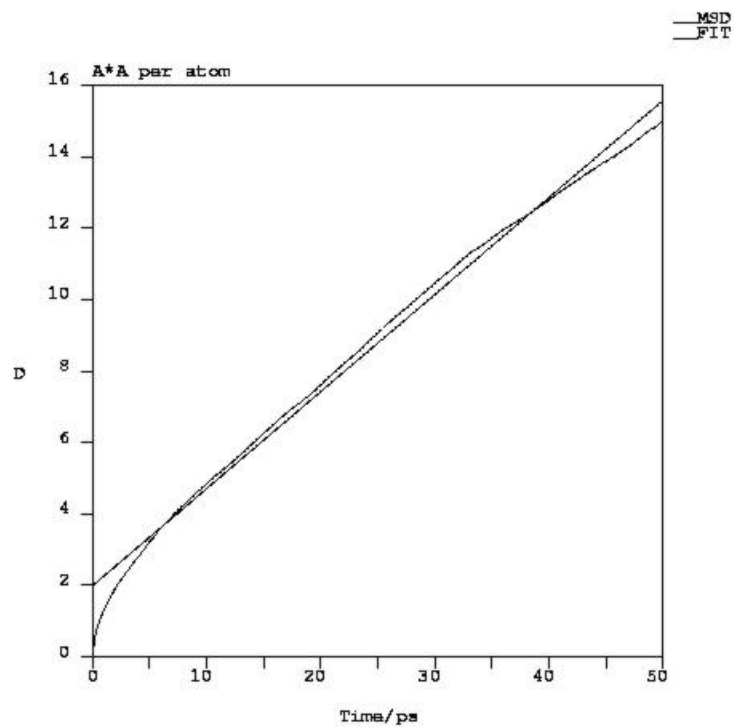
2.1.1. Temperature $T = 300$ K, diffusion coefficient $D = 0.12 \cdot 10^{-5}$ cm²/sec.



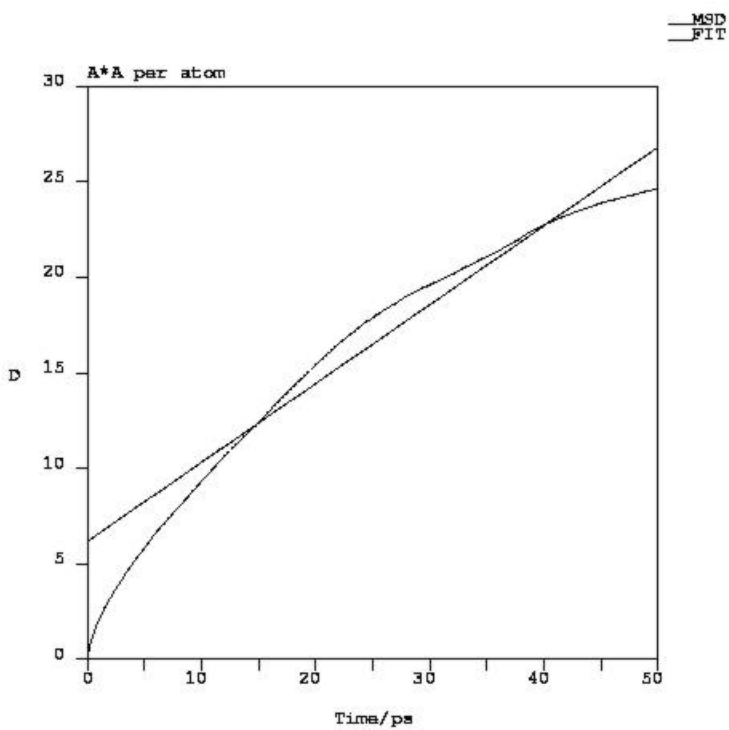
2.1.2. Temperature $T = 360$ K, diffusion coefficient $D = 0.22 \cdot 10^{-5} \text{ cm}^2/\text{sec}$.



2.1.3. Temperature $T = 400$ K, diffusion coefficient $D = 0.44 \cdot 10^{-5} \text{ cm}^2/\text{sec}$.

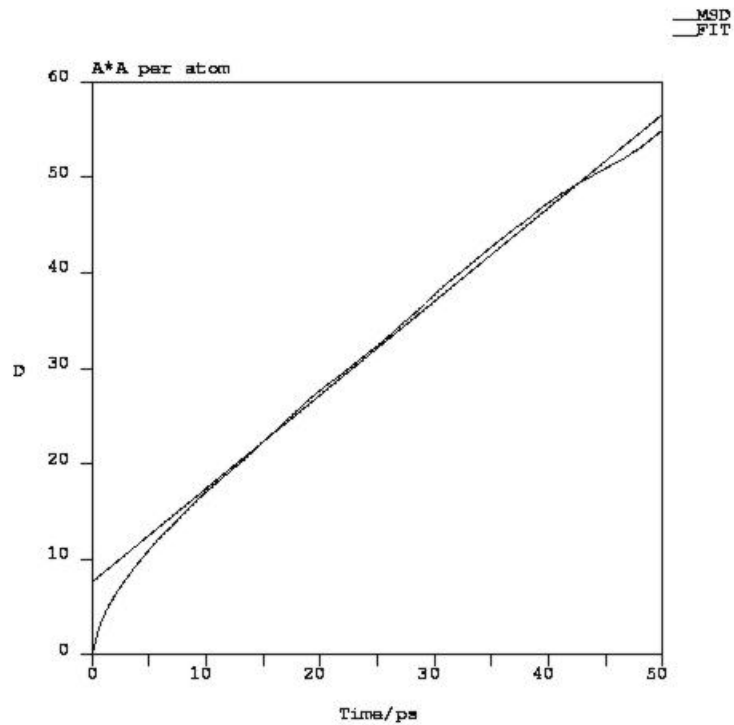


2.1.4. Temperature $T = 450$ K, diffusion coefficient $D = 0.68 \cdot 10^{-5} \text{ cm}^2/\text{sec}$.

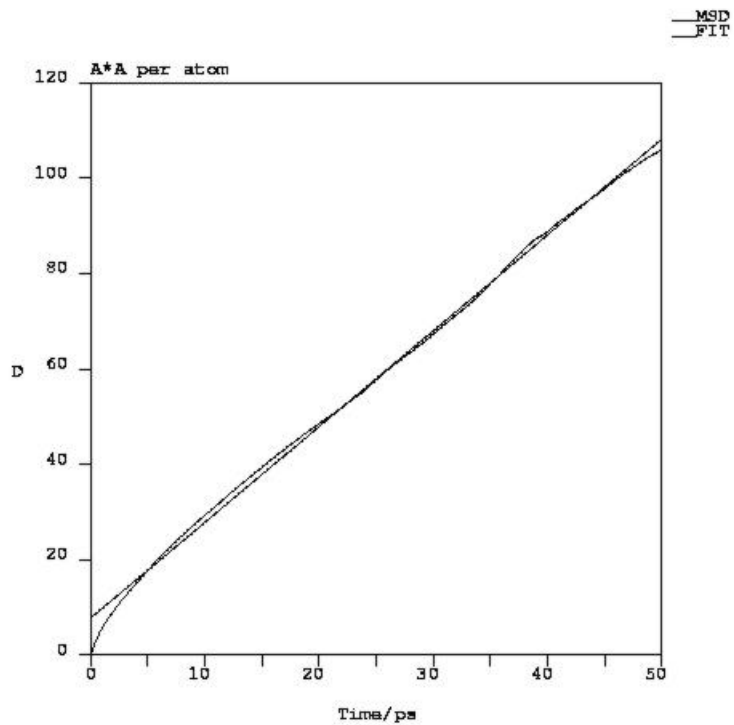


2.2. QAPS-OH membrane with the 14wt% water uptake:

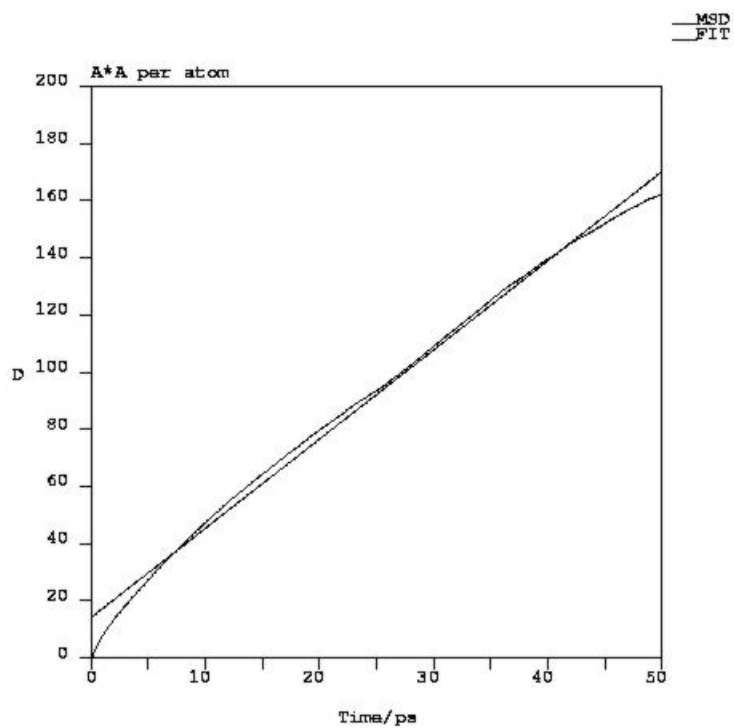
2.2.1. Temperature $T = 300$ K, diffusion coefficient $D = 0.16 \cdot 10^{-4}$ cm²/sec.



2.2.2. Temperature $T = 360$ K, diffusion coefficient $D = 0.34 \cdot 10^{-4}$ cm²/sec.



2.2.3. Temperature $T = 400$ K, diffusion coefficient $D = 0.54 \cdot 10^{-4} \text{ cm}^2/\text{sec}$.



2.2.4. Temperature $T = 450$ K, diffusion coefficient $D = 0.56 \cdot 10^{-4} \text{ cm}^2/\text{sec}$.

